Development of Microbe Cementitious Material in China

RONG Hui (荣  辉), *QIAN Chun-xiang** (钱春香)
als Science and Engineering, Southeast University, Nanii

(School of Materials Science and Engineering, Southeast University, Nanjing 211189, China)

© Shanghai Jiaotong University and Springer-Verlag Berlin Heidelberg 2012

Abstract: Microbe cementitious material as a binder has been developed due to the ever increasing awareness of environmental protection. The new cementitious material relies on microbiologically induced precipitation of calcium carbonate to bind loose particles or repair surface defects and cracks of cement-based material. This paper elaborates the research on loose sand particles cemented by microbe cement from three aspects: compressive strength, pore structure and microstructure. In addition, the research on restoration surface defects and cracks of cement-based material by microbe cement is introduced from two parameters: surface water absorption and compressive strength recover coefficient. The results show that microbe cementitious material can bind loose particles and repair surface defects or cracks of cement-based material.

Key words: microbe cement, defects, microstructure, calcite, cracks

CLC number: TU 526 **Document code:** A

0 Introduction

It is well known that conventional cementitious material mainly includes Portland cement, lime, gypsum, special cement, sodium silicate and so on. However, these man-made chemical materials except sodium silicate are hazardous. For example, Portland cement is a kind of high energy consumption and low "green" material for releasing large amount of $CO₂$ during its production. Therefore, it is required to explore and develop a new alternative cementitious material. In recent years, microbe cementitious material, which consists of alkalophilic microbe, substrate solution and calcium ion solution, has drawn much attention because it is a real "green" material since it relies on the microbial induced formation calcium carbonate precipitation around individual particles and at particle-particle contacts to bind loose particles. To be specific, the cementation process of microbe cementitious material is that the bacteria solution is first introduced into the loose particles and after the solution is fully exudative, numerous bacteria will remain on the surface of particles. Then the mixture of substrate and calcium ion

[∗]**E-mail:** cxqian@seu.edu.cn

solution is injected, and the cementation substance (calcite) will be produced through bio-mineralization. The cementation substance will be attached to the surface of particles, and will enwrap the bacteria as its content increases. Through this process, new calcium carbonate will be formed on the top of older layers, until the adjacent particle grains are connected to form a whole sand body with a certain degree of strength $[1]$. The calcium carbonate induced by microbe cement serves as bridges around particles. At present, microbe cementitious material has been demonstrated in a variety of fields, i.e., the microbe cementitious material can improve the mechanical properties and permeability of porous materials $[2-8]$, enforce or repair cementbased material and limestone^[9-12], modify the properties of soil and sand[3*,*13-14], and enhance oil recovery from oil reservoirs and bioremediation^[15-19]. However, the research is just starting in China. The staffs in Green Construction Material Technology Research Institute of Southeast University have studied correlated projects[20-22]. Now, in order to allow more researchers to understand the progress of microbe cementitious materials in China, it is very necessary to summarize these related researches in detail.

1 Cementation Loose Sand Particles Using Microbe Cementitious Material

1.1 Mechanical Properties and Microstructure

The cylindrical specimens, [∅]30 mm*×*60 mm, are cast to determine the compressive strength. The mix design of the bio-sandstone is as described in Table 1. After

Received date: 2011-11-20

Foundation item: the National Natural Science Foundation of China (No. 51072035), the Ph.D. Program's Foundation of Ministry of Education of China (No. 20090092110029), the Research Innovation Program for College Graduates of Jiangsu Province (No. CXZZ 0145), and the Scientific Research Foundation of Graduate School of Southeast University (No. YBJJ1127)

casting, the specimens are kept at (30*±*2)℃ until

Table 1 Mix design of the bio-sandstone

Constituent	Value
Microbe solution $(4.4 \,\mathrm{mol/L}) / \,\mathrm{mL}$	200
Substrate solution $(2 \text{ mol/L}) / \text{mL}$	100
Calcium ion solution $(2 \text{ mol/L}) / \text{mL}$	100
Quartz sand $/g$	80

testing. After about twenty days, the sample is successfully consolidated.

The compressive strength of representative sandstone cemented by microbe cementitious material can be up to 11.7 MPa , as shown in Fig. $1(a)$. The bio-sandstone sample after failure is shown in Fig. 1(b).

The micrographs of sample are shown in Fig. 2. Most of the microbial induced calcium carbonate crystals seen in Fig. 2 have been precipitated at the surfaces of loose sand particles and between the sand grains.

Fig. 1 Load-deformation curve and failure mode of bio-sandstones

Fig. 2 Scanning electronic micrographs of bio-sandstone

1.2 Micro Porosity and Pore Size Distribution of Bio-sandstone

The pore size distribution of the representative sandstone cemented by microbe cementitious material is measured by mercury intrusion porosimetry (MIP), and the result is shown in Fig. 3. The average pore size in bio-sandstone ranges from 25 to 30 µm. Besides, the micro porosity of loose sand before and after cementation by microbe cement decreases from 43.1% to 23.7%, which shows that treatment with microbe cement can decrease the porosity.

Fig. 3 Pore size distribution of the sandstone cemented by microbe cementitious material

1.3 Macro Porosity of Bio-sandstone Measured by X-Ray Computed Tomography

The 3D defect image of the bio-sandstone is shown in Fig. 4. The bio-sandstone before binding can be seen from Fig. 4(a). The maximum defect volume in biosandstone ranges from 36.75 to 42 mm^3 , which focuses on bottom in bio-sandstone. Figure 4(b) shows the 3D

defect image about bio-sandstone after binding. The result shows the defect volume in bio-sandstone after binding decreases, which ranges from 8.55 to 9.5 mm3. Moreover, other smaller defect volume decreases from 5.25 to 0.95 mm3. The macro porosity about this specimen before and after binding varies from 6.06% to 2.12%.

Fig. 4 Defect images of bio-sandstone

2 Restoration Surface Defects of Cement-Based Materials Using Microbe Cementitious Material

Cement paste samples made with Portland ordinary cement 32.5 and 0.45 water-cement ratios are cast into 30 mm*×*30 mm*×*30 mm mould. After casting, the specimens are cured at room temperature for 7 days. Large number of bacteria will be absorbed on the surface of cement paste by multiple brushing of microbe cement so that microbial induced formation of calcite is precipitated on the surface defects of cement paste. The specific ways are shown in Fig. 5. The high concentration bacteria cell is firstly brushed on the bottom layer of cement paste, and then the substrate and Ca^{2+} ions are brushed on the middle layer. Finally, the high concentration bacteria cell is brushed on the top layer again. After brushing, the specimen is cured at room temperature to observe restoration effectiveness. The result shows that the surface of cement paste has a layer of white precipitation substances after 3 days. After curing for 7 days, there are lots of dense white precipitation substances on the surface, as shown in Fig. 6. The white precipitation substances are analyzed by energy dispersion spectroscopy (EDS), showing that there are three elements of carbon, oxygen and calcium (Fig. 7). Meantime, the X-ray diffraction (XRD) result of Fig. 8 shows that the white precipitation is calcite; θ is the Bragg angle of diffraction peak.

Figure 9 shows the film effectiveness on the surface of cement paste. It can be seen from Fig. 9 that calcite grains have formed a layer of film covered on the surface so that pores in the surface of cement paste are plugged. The formation of calcite film on the surface can prevent water and harmful substances into the cement paste. In addition, from Fig. 9 it can be observed that the thickness of calcite film is about $100 \,\mu m$. In addition, the restoration effectiveness of surface defects is characterized by the decreased coefficient of water absorption of surface. The water absorption of surface can be decreased of 85% by this brushing method.

Fig. 5 Brushing methods of bacteria on specimen surface

(a) Untreated specimen (b) Treated specimen

Fig. 6 The specimen with bacterially deposited layer on its surface

Fig. 7 Energy dispersive spectrum of the deposited layer on the specimen surface

Fig. 8 X-ray spectra of the deposited layer on the specimen surface

Fig. 9 Scanning electronic micrographs of the calcite layer on specimen surface

3 Restoration Cracks of Cement-Based Materials Using Microbe Cementitious Material

Cement paste samples made with Portland ordinary cement 32.5 and 0.45 water-cement ratios are cast into $50 \text{ mm} \times 50 \text{ mm} \times 50 \text{ mm}$ mould. After curing of 7 days at room temperature, the crack, 3 mm width and 20 mm depth, is cut to restore. Then the high concentration bacteria according to a ratio are mixed with loose sand, substrate and $Ca(NO₃)₂$ to inject into the crack of cement paste. In order to better characterize the restoration effectiveness, the biggest compressive strength of loss area is chosen in this subject, as shown in Fig. 10. The restoration effectiveness of cracks is characterized by the compressive strength recovery

coefficient (G) and the compressive strength increasing coefficient (H) . The experimental results are shown in Table $2^{[22]}$. S₁ group only contains urea, loose sand and Ca^{2+} ions. Therefore, the values of G and H are only 65% and 36%, respectively. S₂ group not only contains urea, loose sand and Ca^{2+} ions, but also contains microbe. So the values of G and H can respectively reach 84% and 76% due to the formation of calcite induced by microbe cement. C_0 denotes the original cubes; C_1 denotes the cracked cubes after restoration; $C₂$ denotes the cubes after cracked. Figure 11 shows the microstructure of specimen after crushing. From Fig. 11 it can be observed that most of the microbial induced calcium carbonate crystals have been precipitated at the surfaces of loose sand particles and between the sand grains. This can bind loose sand to the whole body for filling the cracks of cement paste so that the cracks can be repaired and the compressive strength can be improved.

Table 2 Compressive strength of cement specimens after crack-restoration

Group		Compressive strength/MPa			G
	C_0	C ₁	C_2		
S ₁	15.42	10.07	7.39	0.36	0.65
S_2	15.42	13.01	7.39	0.76	0.84

Fig. 10 Position of cracks when specimen under pressure

(a) Sands covered by CaCO₃ particles (b) Sands cemented by CaCO₃ particles

Fig. 11 Scanning electronic micrographs of sand cementation in cracks of cement specimen

4 Conclusion

The development of cementation loose particles, restoration surface defects and cracks of cement-based material using microbe cement in China is summarized in this paper. The results obtained in this work can be summarized as follows.

(1) The feasibility of microbe cement cementation loose particles and restoration defects or cracks of cement-based material is determined.

(2) The mechanical properties of sandstone cemented by microbe cement are very excellent. The degree of improvement mainly depends on the microbial induced precipitation calcium carbonate content and porosity.

(3) The surface defects and cracks of cement-based material can be restored by microbe cement. The restoration effectiveness depends on the film coving modes of surface, width and depth of cracks and so on.

(4) The application filed of microbe cementitious material does not appear to be limited to the small samples. Microbe cement will apply to other filed in the future, e.g., foundation reinforcement and desertification control.

References

- [1] Qian C X, Pan Q F, Wang R X. Cementation of sand grains based on carbonate precipitation induced by microorganism [J]. *Science China Technological Sciences*, 2010, **53**(8): 2198-2206.
- [2] MÉTAYER-LEVREL G L, CASTANIER S, ORIAL G, et al. Applications of bacterial carbonatogenesis to the protection and regeneration of limestones in buildings and historic patrimony [J]. *Sedimentary Geology*, 1999,

126: 25-34.

- [3] NEMATI M, VOORDOUW G. Modification of porous media permeability, using calcium carbonate produced enzymatically in situ [J]. *Enzyme and Microbial Technology*, 2003, **33**: 635-642.
- [4] Dejong J T, Fritzges M B, Nusslein K. Microbially induced cementation to control sand response to undrained shear [J]. *Journal of Geotechnical and Geoenvironmental Engineering*, 2006, **132**: 1381-1392.
- [5] Dejong J T, Mortensen B M, Martinez B C, et al. Bio-mediated soil improvement [J]. *Ecological Engineering*, 2010, **36**: 197-210.
- [6] WHIFFIN V S. Microbial $CaCO₃$ precipitation for the production of Biocement [D]. Western Australia: School of Biological Sciences and Biotechnology, Murdoch University, 2004.
- [7] Whiffin V S, van Paassen L A, Harkes M P. Microbial carbonate precipitation as a soil improvement technique [J]. *Geomicrobiology Journal*, 2007, **24**: 417- 423.
- [8] Ivanov V, Chu J. Applications of microorganisms to geotechnical engineering for bioclogging and biocementation of soil in situ [J]. *Review Environmental Science Biotechnology*, 2008, **7**: 139-153.
- [9] Muynck W D, Belie N D, Verstraete W. Microbial carbonate precipitation in construction materials: A review [J]. *Ecological Engineering*, 2010, **36**: 118- 136.
- [10] Muynck W D, Verbeken K, Belie N D, et al. Influence of urea and calcium dosage on the effectiveness of bacterially induced carbonate precipitation on limestone [J]. *Ecological Engineering*, 2010, **36**: 99-111.
- [11] Muynck W D, Debrouwer D, Belie N D, et al. Bacterial carbonate precipitation improves the durability of cementitious materials [J]. *Cement Concrete Research*, 2008, **38**: 1005-1014.
- [12] Qian C X, Wang J Y, Wang R X, et al. Corrosion protection of cement-based building materials by surface deposition of $CaCO₃$ by Bacillus pasteurii [J]. *Materials Science and Engineering C*, 2009, **29**: 1273- 1280.
- [13] Nemati M, Greene E A, Voordouw G. Permeability profile modification using bacterially formed cal-

cium carbonate: Comparison with enzymic option [J]. *Process Biochemistry*, 2005, **40**: 925-933.

- [14] RONG H, QIAN C X, LI L Z. Influence of molding process on mechanical properties sandstone cemented by microbe cement [J]. *Construction and Building Materials*, 2012, **28**: 238-243.
- [15] FERRIS F G, PHOENIX V, FUJITA Y, et al. Kinetics of calcite precipitation induced by ureolytic bacteria at 10 to 20 ℃ in artificial groundwater [J]. *Geochimica et Cosmochimica Acta*, 2003, **67**(8): 1701-1722.
- [16] Fujita Y, Ferris F G, Lawson R D, et al. Calcium carbonate precipitation by ureolytic subsurface bacteria [J]. *Geomicrobiology Journal*, 2000, **17**(4): 305-318.
- [17] Warren L A, Maurice P A, Parmar N, et al. Microbially mediated calcium carbonate precipitation: Implications for interpreting calcite precipitation and for solid-phase capture of inorganic contaminants [J]. *Geomicrobiology Journal*, 2001, **18**(1): 93-115.
- [18] CHATURVEDI S, CHANDRA R, RAI V. Isolation and characterization of Phragmites australis (L.) rhizosphere bacteria from contaminated site for bioremediation of colored distillery effluent [J]. *Ecological Engineering*, 2006, **27**: 202-207.
- [19] Simon M A, Bonner J S, Page C A, et al. Evaluation of two commercial bioaugmentation products for enhanced removal of petroleum from a wetland [J]. *Ecological Engineering*, 2004, **22**: 263-277.
- [20] Qian C X, Wang R X, Cheng L, et al. Theory of microbial carbonate precipitation and its application in restoration of cement-based materials defects [J]. *Chinese Journal of Chemistry*, 2010, **28**(5): 847-857.
- [21] Wang Rui-xing, Qian Chun-xiang. Restoration of defects on the surface of cement-based materials by microbiology precipitated CaCO³ [J]. *Journal of the Chinese Ceramic Society*, 2008, **36**(4): 457-464 (in Chinese).
- [22] Wang Jian-yun, Qian Chun-xiang, Wang Rui-xiang, et al. Application of carbonate-mineralization bacterium in surface protection of cement-based materials [J]. *Journal of the Chinese Ceramic Society*, 2009, **37**(7): 1097-1102 (in Chinese).